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ARL 63-134

STUDIES ON THE DECOMPOSITION OF NITROUS OXIDE

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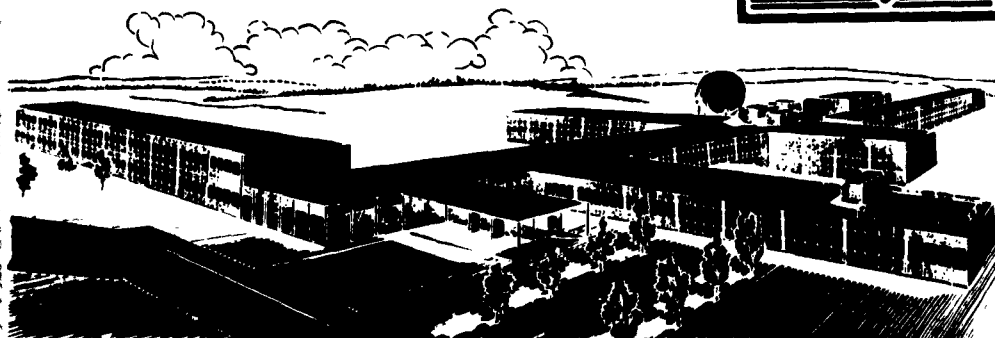
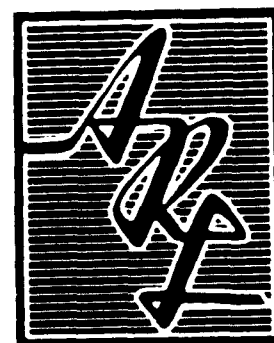
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ARL 63-134

STUDIES ON THE DECOMPOSITION OF NITROUS OXIDE

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ABSTRACT

Two experimental facilities for the investigation of the rate and mechanism of the decomposition of nitrous oxide are described. One facility, a combustion driven shock tube, is designed to provide information on the rate of decomposition at temperatures to 3000°K and pressures to 200 atm. Preliminary results on the rates at several temperatures are reported. For example, a half-life of 31 μsec was determined for the nitrous oxide decomposition in argon-nitrous oxide mixtures at 2210°K . The other facility is designed to provide information on the decomposition process and products in a flowing nitrous oxide system. Preliminary results indicate that the decomposition below 900°K proceeds very slowly as reported by other investigators. One rather interesting result indicates that the decomposition rate in a flowing gas system is quite sensitive to temperature gradients and hot spots in the heating system. At 923°K the decomposition proceeded very rapidly and only 4% nitrous oxide remained after about 2 seconds.

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SECTION I. INTRODUCTION

The laboratory simulation of flight conditions during re-entry into the earth's atmosphere is extremely difficult. One of the best aerodynamic tools for this simulation is the high-speed wind tunnel. Although existing facilities provide certain basic information concerning re-entry conditions, they are limited because of the relatively low stagnation temperatures which can be obtained. The basic problem concerns the maximum temperature at which the heating elements can be operated. With existing heating elements the maximum Mach number which can be obtained is about 18-20. But these Mach numbers entail gas flows whose static temperatures are quite low; hence, the velocity of the gas is not as high as desired. The basic concern, then, is the generation of high stagnation temperatures. It is in this area that nitrous oxide plays an important role.

Nitrous oxide releases about 20,000 cal/mole upon decomposition into $N_2 + 1/2 O_2$. This energy is sufficient to increase the temperature of the decomposition products by about 2000°K. From data by Hunter (Ref. 1) it appears that a self-sustaining decomposition may be obtained if the gas were heated to about 1100 - 1200°K initially. The final temperature of the products would be about 2500 - 3000°K. One further point is that the decomposition products would be similar to air. To obtain the nitrogen to oxygen ratio of air a small amount of nitrogen should be added to the nitrous oxide. But even then the stagnation temperature would be higher so that the range of present wind tunnels could be extended.

To understand the conditions under which the nitrous oxide may be used more information is needed on the reaction times at temperatures to 3000°K and also on the products of decomposition when the gas is flowing. The flowing decomposition is quite interesting since it provides a method whereby the reaction times and product species may be determined for a constant pressure decomposition.

This report describes two separate experimental facilities devoted to a detailed study of the rate and mechanism of decomposition of nitrous oxide. The first facility consists of a shock tube which was constructed to provide data concerning the rate of decomposition of nitrous oxide to 3000°K. The second facility was designed primarily to study the decomposition in a flowing system similar to the heating section of a wind tunnel.

SECTION II. REACTION KINETICS

A technique has been developed whereby the rate and mechanism of the decomposition of nitrous oxide may be determined experimentally. This

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technique is applicable in the temperature region above approximately 1200°K. Extrapolation of the low temperature data obtained by Hunter (Ref. 1) to a temperature of 1500°K reveals that the half-life of the nitrous oxide should be about 500 μ sec. Obviously, such fast rates require special techniques to heat the gas uniformly and rapidly if meaningful measurements are to be obtained. Shock waves have been used by many investigators to provide uniform and rapid heating of gaseous systems. The experimental application of shock waves for the study of fast reaction times has been discussed rather completely by Ferri (Ref. 2). To obtain the required shock waves a combustion driven shock tube has been designed and constructed.

Once the gas has been heated some technique must be devised to follow the rate of decomposition of nitrous oxide. In the present facility the concentration of the hot nitrous oxide is followed by means of infrared absorption and emission techniques. Since the nitrous oxide molecule is triatomic and heteronuclear, it has several vibration-rotation bands in the infrared. We may follow the nitrous oxide decomposition by studying either the infrared absorption or emission of one of these bands.

1. SHOCK TUBE FACILITIES

The shock tube to be used in this study is constructed entirely of stainless steel. The driver section is 17' long, has an internal diameter of 3", and a wall thickness of 1". The length of the driver section must be such that the expansion wave, which travels into the driver gas upon rupture of the diaphragm, must not reflect from the end of the tube and overtake the contact surface (driver gas-driver gas interface) before the contact surface reaches the testing area. Such an arrangement provides a maximum of testing time with a given driven section length. The driven section is 20' long, has an internal diameter of 3-1/4", and a wall thickness of 3/8". A dump tank is located at the end of the driven section and is designed so that the shock wave, upon reflection at the end of the tube, will not return to the testing area before the contact surface arrives. Again such an arrangement provides a maximum of testing time.

The driver section is filled with a combustible mixture through seven gas inlets. Each gas inlet consists of 4 small orifices designed to introduce the gas with a swirling motion thereby producing a more uniform mixture of the combustible gases in the driver section. The combustible mixture is ignited at 17 locations in the driver section. These ignitors consist of exploding wires and are uniformly distributed throughout the driver section. Initially .005" silver wire was used as the ignitor wire and was exploded by a 250 V-DC potential. However, the current surge was extremely large and induced voltages in the electronic instrumentation which produced erratic results. At the present time Pyrofuze ignitor wire is used and is ignited by a 6 volt battery. Since a smaller current is required to explode the Pyrofuze wire, only a negligible voltage is induced in the electronic instrumentation.

The velocity of the shock wave is determined at a point midway down the driven section and at the end of the tube, before the dump tank, where the infrared detection system is located. Initially, pressure transducers were used to detect the passing of the shock wave. The signals from these transducers were used to start and stop 10-megacycle chronographs which then displayed the time necessary for the shock wave to travel from one transducer to the other. The shock velocity was obtained by dividing the distance between these transducers by the time displayed on the counters. The measurement of shock velocity at two points revealed that the velocity attenuation was negligible in the region of shock speeds of interest.

During the calibration of the shock tube instrumentation high pressure air was used in the driver section instead of a combustible mixture. Mylar diaphragms were used and were ruptured by increasing the air pressure in the driver section. The results obtained during this calibration phase were quite encouraging. Particularly encouraging were the responses of the pressure transducers. However, when the shock wave was generated by expanding the burned gases, the excessive vibration of the shock tube caused by the instantaneous combustion triggered the instrumentation each time. Therefore, it became necessary to investigate other ways of determining the shock velocity. Of particular interest was the use of high speed temperature sensing devices.

Considerable effort by various investigators has been devoted to the use of thin platinum strips as temperature sensing devices. These strips are obtained by brushing a liquid containing colloidal platinum onto some electrically nonconducting body such as pyrex. The pyrex is heated to evaporate the liquid thereby leaving the platinum. The resistance of the strips can be controlled by varying the amount of platinum deposited. A resistance of about 100 ohms has been found to provide a good electrical output and a fast response. Electrical leads are soldered to the strips and a working current of about 30 milliamperes is used. The high temperature behind the shock wave causes the resistance of the strip to increase in less than one microsecond. Since the strip is located in one part of a bridge network, a change in resistance produces a change in voltage drop across the strip. This change in voltage drop across the strip is the signal which triggers the instrumentation.

The major advantage of the platinum strips to determine the shock wave velocity is that it is necessary for a temperature increase to occur before a signal is obtained. One problem, mentioned earlier, which existed with the platinum strips was that any changing magnetic field induced a voltage in the leads to the strip. Because of the rather large amplification these spurious signals triggered the equipment. However, with the use of Pyrofuze wire and a low voltage these spurious signals were reduced to a negligible level. At the present time only a minor problem exists. When the hot driver gases arrive at the strip they tend to melt the solder connection between the strip and the lead wire. However, this is only a minor problem and requires resoldering the connections frequently.

2. INFRARED SENSING SYSTEM

The techniques of infrared spectroscopy offer a convenient method of following the relative concentration of reacting species. Every polyatomic molecule has an infrared spectrum. In the particular case of nitrous oxide three fundamental vibration-rotation infrared bands exist (Ref. 3). The band at 16.9μ corresponds to the bending vibrational mode which is the easiest to excite. The symmetric valence mode has its fundamental band at 7.78μ and is more difficult to excite than the bending mode. The asymmetric valence mode has its fundamental band at 4.49μ and is the most difficult to excite vibrationally. Many overtone bands and intercombination bands are found throughout the intermediate infrared. Initially the asymmetric mode was employed since it was located in a spectral region readily obtainable with conventional infrared detectors. Although this mode is the last to relax, it may be expected that it will relax prior to dissociation, especially at the lower temperatures.

In the beginning of the experimentation a lead telluride detector was used because of the fairly large resistance of the detector. It can be derived from simple circuit analysis that for a constant current the signal voltage is directly proportional to the change in resistance of the detector. The major disadvantage of this detector was its fairly slow response time. If the response time were based on the RC time constant of a resistance-capacitance circuit then the RC time constant for the detector would be $90\ \mu\text{sec} \pm 3\ \mu\text{sec}$. In spite of this long response time it was felt that this detector should be used until all of the peculiarities of the system had been mastered.

Absorption spectroscopy was to be used since at the temperatures of interest in this study the gas probably would not radiate sufficiently. The particular optical arrangement is shown in Figure 1. Radiation from a Nernst glower is directed through two sapphire windows in the tube wall and onto a mirror mounted on the shock tube. The radiation then is reflected to a second mirror mounted on the monochromator and into the entrance slit of the monochromator. These two mirrors are mounted so that the radiation reflected from the first mirror travels exactly parallel to the shock tube. In this manner any longitudinal movement of the shock tube, occurring when the diaphragm bursts, would not affect the intensity of radiation entering the monochromator. These mirrors are rigidly supported so that they would not be affected by vibrations of the tube. Radiation of the desired wavelength leaving the monochromator is directed onto the infrared detector by a concave mirror. The infrared detector has been installed on a micrometer mount which permits optimum alignment of the detector.

As mentioned above absorption techniques were used originally. However, it soon was realized that the emission from the gas was completely masking the absorption. The use of emission techniques greatly simplifies the analysis if compensation can be made for the effects of vibrational relaxation. This compensation is made in two

ways. The particular infrared band which is now being used is located at about $3.8 - 3.9\mu$. This is an intercombination band involving the bending mode and the symmetric mode. As the symmetric mode relaxes, the intensity of the radiation should increase because of the increased population density of the higher symmetric vibrational levels. As the nitrous oxide decomposes, the radiation intensity should decrease. These suppositions are based on no change in pressure or temperature behind the shock wave. Energy is released with the decomposition of nitrous oxide so that the temperature of the gas increases. From Rayleigh line considerations it is found that with a temperature increase the pressure should decrease. Thus we have a gaseous region in which both temperature and pressure are changing each imposing opposite effects on the radiation (increase in temperature increases intensity while decrease in pressure decreases intensity). Including the effects of the decomposition of nitrous oxide the interpretation of the rate of change of radiation intensity presents a formidable problem. To alleviate this situation it was decided to study initially the rate of decomposition of nitrous oxide diluted with argon. For a mixture containing 98% argon any energy released by the decomposing nitrous oxide would be small. It has been found that argon is 40% as efficient in the transfer of energy to the nitrous oxide molecule as another nitrous oxide molecule. Even if this figure were in error the correct value would be determined when the initial rate of decomposition of pure nitrous oxide mixtures were studied. It is advantageous to use argon because its effect on the reaction is independent of temperature (in the region of interest). At the present time the rate of decomposition of nitrous oxide in a mixture containing 95% argon is being studied.

In the argon-nitrous oxide mixtures no nitric oxide is expected to form since most researchers believe that nitric oxide is formed by the reaction $N_2O + O \rightarrow 2NO$. If nitric oxide is found in argon-nitrous oxide mixtures then it must be formed in the thermal decomposition process. Once the argon-nitrous oxide mixtures have been studied in detail it is intended to study the rate of formation of nitric oxide in pure nitrous oxide.

It has been found necessary to clean the shock tube after every second experiment. Contamination builds up which may radiate quite strongly. After cleaning the tube an experiment was conducted with pure argon to study the level of contaminant radiation. In this particular experiment the gas temperature was $4700^\circ K$. The contaminant radiation was quite low and remained at a constant level. At the lower temperatures and higher gas pressures this contaminant radiation should not affect the results.

3. RESULTS

The results of three experiments are shown in Figure 2. This figure shows only representative traces obtained of the variation of radiation intensity. The first trace was obtained with the lead telluride detector and the radiation was emanating from an argon-nitrous oxide mixture at

1160°K and 6.2 atm. Note the rise time and constant value of radiation intensity. In this experiment the decomposition was too slow to be recorded. The second trace was also obtained with the lead telluride detector and the gas mixture was at 1440°K and 7.8 atm. Note the decay of the radiation indicating rapid decomposition. The point of maximum radiation can be related directly to the rate of decomposition. In this experiment the half-life was found to be 1140 μ sec. Of course, this half-life corresponds to argon-nitrous oxide collisions. The third trace was obtained with an indium antimonide detector. Note the difference in the response times. The gas temperature and pressure was 2100°K and 16.3 atm., respectively. In this experiment the half-life of the nitrous oxide was 48 μ sec.

Table I contains a summary of data collected to date. In these experiments the concentration of nitrous oxide was 4.63% by volume. From these data some preliminary conclusions may be made concerning the rate of decomposition in argon-nitrous oxide mixtures. If a first order reaction is assumed the rate of decomposition of nitrous oxide is given by

$$\frac{d(N_2O)}{dt} = -K(N_2O)$$

where (N_2O) is the nitrous oxide concentration and K is the reaction rate constant given by

$$K = A \exp \left(- \frac{E}{RT} \right)$$

where E is the activation energy in cal/mole, R is the universal gas constant, T is the temperature in °K, and A is the frequency factor. Combining these two equations the following relation is obtained between the half life of the nitrous oxide and the temperature

$$\ln t_{1/2} = \ln \left(\frac{.693 \times 10^6}{A} \right) + \frac{E}{RT}$$

where t is measured in microseconds. Thus a graph of $\ln t_{1/2}$ vs T^{-1} should produce a straight line whose slope is E/R. The data collected thus far is presented in this manner in Figure 3. Note that these data may be represented by a straight line quite readily. From this graph the following reaction rate constant is obtained

$$K = 7.9 \times 10^8 \exp \left(- \frac{45,600}{RT} \right)$$

Any comparison between the rate constant above and that obtained by Hunter (Ref. 1) must be delayed until further experiments, especially those with pure nitrous oxide, are conducted. However, at this point in the study the decomposition rate does not appear to be effected by pressure which indicates a first order reaction.

SECTION III. DECOMPOSITION OF FLOWING NITROUS OXIDE

Studies of the decomposition of nitrous oxide at constant volume have been conducted by various investigators (Refs. 1, 4-7). In addition, constant pressure decompositions have also been considered (Refs. 7-9); however, experimental studies of the exact processes involved in the constant pressure process have not been considered, i.e., rate of nitrous oxide decomposition and nitric oxide formation as a function of experimental conditions such as initial pressure, temperature and gas flow rate, at various times in the reaction. This information is desired in order to determine the maximum temperature which can be achieved in conjunction with a minimum amount of nitric oxide formation.

Methods of initiating the decomposition which were considered are electrothermal heat addition and direct addition of energy to the stream using an electric arc process. It was decided to initiate the reaction by the former method. Investigation into the use of an electric arc at elevated pressures indicates that arc stability problems would necessitate the expenditure of a rather considerable amount of effort in the development of a stabilized arc discharge. In addition, the power supply requirements at elevated pressures become quite stringent, and would require power inputs in excess of the total power capacity that is available at this laboratory.

1. EXPERIMENTAL APPARATUS

The basic purpose underlying the design of the experimental apparatus was to obtain overall reaction rates, reacted gas temperatures, and composition of the reaction products for various initial pressures and temperatures and various flow rates of pure nitrous oxide and additives. The equipment was designed for pressures up to 200 atmospheres.

The reaction vessel is illustrated in Figure 3; it consists of a 10-3/4 inch O.D. by 8-1/2 inch I.D. stainless steel pipe, 10 feet long. Stainless steel flanges, 18 inches in diameter by 2-1/2 inches thick provide access to the internal heaters and reaction chamber sections.

The heated section consists of 4 one-foot long alumina tubes, 1 inch I.D. with a 1/8 inch wall. The alumina tubes are wrapped circumferentially with approximately 90 turns of .040 inch Kanthal A-1 resistance wire. This wire has a maximum operating temperature of approximately 1600°K. The wire is covered with an alumina cement to provide structural support for the wire, and to provide the maximum possible heat transfer from the wire to the tube surface. Total power dissipation of each of the four heater sections with 220 V-AC applied is approximately three kilowatts.

The wall temperatures are controlled by a Simplytrol thermocouple actuated temperature controller. The schematic diagram is shown in Figure 4. The chromel/alumel sheathed thermocouples used for the heater temperature control are imbedded in the external surface of the ceramic cement heater wire coating. A thermocouple is placed at the downstream end of each of the heater sections. The percentage on-time of the heaters during a given demand cycle is controlled by means of conventional percentage timers. This permits control of the rate of power input into the system at constant supply voltage. The effects of thermal overshoot are minimized by this technique.

The ceramic heater sections are located coaxially inside a 4-7/8 inch I.D. by 5-1/4 inch O.D. stainless steel tube. The tubes are supported by Fiberfrax board. Loose Fiberfrax is packed into the volume between the heater and the 5-1/4 inch O.D. stainless steel tube to reduce the heat loss to the external surroundings.

The reaction tube sections are assembled like the heater sections. The alumina tubes used in the reaction tube sections are composed of a higher purity alumina to allow a maximum usable temperature of approximately 2200°K. The reaction tubes are geometrically similar to the alumina tubes used in the heater sections; however, they have 1/4 inch thick walls. In addition, the reaction tube sections have no Kanthal wire wrapped around the external surface of the alumina tube. The reaction section consists of 5 individual sections, making a total reaction chamber length of 5 feet. The total length of the heater sections and reaction chamber is 9 feet.

The heater and reaction chamber assembly is mounted on the centerline of the large stainless steel pressure vessel. Nitrous oxide is introduced into the center of the alumina tubes at the upstream end. The gas flow is injected tangentially through 4 ports to insure a turbulent flow through the heaters. This method provides a good heat transfer rate from the walls to the flowing nitrous oxide stream. Based on the inside diameter of the ceramic tubes, Reynolds numbers of approximately 25,000 are obtained at the exit of the heater section.

Cooling air is passed through the annular space between the internal wall of the pressure vessel and the surface of the heater and reaction tube assembly. This annular air flow prevents overheating the pressure vessel walls. Mixing of the cooling air flow and the reacting gas flow occurs before the exhaust port, thereby reducing the total temperature of the exhaust flow. A heat exchanger is used to further reduce the temperature of the exhaust gases.

A fixed orifice size was originally used to restrict the pressure vessel exhaust gases. It was found, however, that this arrangement was unsatisfactory. The combined effects of the increased temperature and volume flow rate due to the decomposition could not be adequately eliminated to maintain a constant internal pressure. A variable restriction was installed in the exhaust line. This consists of a

pneumatically operated Annin valve. The effective orifice area can be adjusted by regulation of the operating pressure on the valve.

A glass window with a clear opening 1 inch in diameter is located on the upstream flange. This provides optical visualization of the internal heaters and reaction chamber. Optical pyrometer measurements of temperatures of the internal walls of the heaters and probe are made through this window.

Gas temperatures and gas samples are obtained with a water-cooled probe which can be moved axially through the length of the reaction chamber and heater assembly. The total probe length is 12-1/2 feet. The outside diameter of the stainless steel probe is .625 inch, with a wall thickness of .040 inches. A 3/8 inch diameter tube, .020 inch wall thickness, is placed coaxially internally to provide a cooling water supply and return to the forward end of the probe. Hypodermic tubing .040 inch in diameter is used to withdraw the gas sample from the forward tip of the probe to the external connection. Rapid quenching of the reaction is insured by the low flow rates through the hypodermic tubing and the water cooling. Gas temperatures are measured with a tungsten/tungsten-26% rhenium thermocouple. The unique design of this thermocouple permits remaking the hot junction if an open connection or a burnout occurs. The thermocouple element consists of wafers of tungsten and tungsten-26% rhenium separated by a thin wafer of mica. The output leads of the thermocouple elements are welded to copper extension leads. The extension leads are enclosed in a 1/8-inch diameter stainless steel sheath packed with magnesium oxide. The stainless steel sheath is brazed to the 3/16 inch tantalum sheathed thermocouple element to provide a continuous pressure tight thermocouple unit. The hot junction is obtained by grinding the tip of the thermocouple. The resulting burring of each of the wafer thermocouple elements make the hot junction.

A black body target is installed on the forward tip of the probe. This target is cast from Astro-Ceram Type A high temperature ceramic cement, with a cavity 1/8 inch in diameter and approximately 1 inch deep. This target also serves to withdraw the gas sample from the same axial location as the thermocouple temperature measurement is being made. The tantalum sheath and copper probe tip are coated with the Astro-Ceram Type A cement to provide resistance to chemical attack by the nitric oxide and oxidization of the surfaces at the elevated temperatures.

The samples are withdrawn from the reaction tube into evacuated 250 ml pyrex flasks. The samples are withdrawn directly into the evacuated flasks until the pressure in the flasks is slightly above atmospheric pressure. The flasks are then flushed until the gas volume has been changed approximately 15 times. This virtually eliminates the presence of air in the mixture. The flasks are initially evacuated to an absolute pressure of 50 microns or less. The samples are analyzed chromatographically.

Various methods of chromatographically determining the composition of mixtures of nitrogen, oxygen and the oxides of nitrogen (i.e., nitric oxide, nitrogen dioxide and nitrous oxide) are given in Refs. 10-13. The reactivity of the nitric oxide in the presence of oxygen makes the complete analysis of mixtures of these gases extremely difficult by gas chromatography. At present, there is no known column material that will directly separate all of the constituents of mixtures including nitric oxide and nitrogen dioxide in the presence of oxygen. An alternative method of analysis of mixtures which include nitric oxides is to freeze out the nitrogen dioxide before introducing the gas sample into the chromatograph. The method used for this analysis is presented in the appendix.

The gas chromatographic equipment used for this analysis is an F and M Scientific Corporation Model 500 Linear Temperature Programmed Gas Chromatograph. This instrument permits programming the separation column temperature at linear rates from .2 to 42°C per minute. At the higher rates, maximum heater power considerations limit the linear rate to a temperature region below 200°C; however, this provides adequate control to permit good repeatability of the time dependent column temperature curve. The column packing material used for all analysis is Molecular Sieve 5A. This material separates nearly all permanent gases (i.e., H₂, O₂, N₂, CO₂, N₂O, Ne).

The output of the chromatograph is recorded on a conventional Brown potentiometric strip chart recorder. The recorded output produces a nearly Gaussian curve. The area between this curve and the baseline is proportional to the amount of the constituent in the sample. A Disc integrator is connected to the recorder to provide a continuous integration of this area with time. In addition, the integrator has a rotary switch which provides 40 switching operations per rotation of the integrator shaft. This switch, when used in conjunction with a counter, provides a direct indication of the area under the output curve.

A special gas mixture consisting of 31.7 percent by volume of oxygen, 33.5 percent by volume of nitrogen, the balance being nitrous oxide, is used to calibrate the chromatograph. This procedure provides a convenient means of determining the correction factors to be applied to the linear relationships between volume and the area under the curve. This information is necessary since the use of direct area ratios would imply that all gases have identical thermal conductivities.

The nitrous oxide used for these experiments was obtained from commercial sources. A nitrous oxide liquifaction transfer and storage system described in Ref. 4 was used to provide high-pressure nitrous oxide for these experiments. The liquifaction-vaporization process was also used to purify the nitrous oxide. Withdrawal of the gases above the liquid nitrous oxide virtually eliminates all impurities. The primary impurity in nitrous oxide, according to the Matheson Company, consists of 1 to 2 percent nitrogen; however, samples of the nitrous oxide supply taken at various times showed that the nitrogen content amounted to only .1 percent or less.

A conventional flow control system is used to meter the nitrous oxide and the flow rates of the cooling air. Maximum pressure capability of this system is 3000 psi. Flow rates of 3 liters per second can be obtained with both systems. The lines carrying the nitrous oxide from the supply tank to the flow control panel and to the reaction vessel inlet are wrapped with an electrical heater wire. To avoid condensation, it is necessary to maintain the nitrous oxide above 93°F (its critical temperature). A pebble bed heater was used to reheat the nitrous oxide after its expansion which brought the temperature below the critical point.

2. RESULTS AND CONCLUSIONS

Experiments were conducted to determine the heat transfer properties of the heater sections to an internal air flow. At air flow rates up to 3 liters/second, the heaters appeared to be nearly 100 percent efficient. Due to non-equilibrium temperature gradients and thermal over-shoot, the air temperature at the exit of the heater was on occasion higher than the set wall temperature. It was found that elimination of these effects made it necessary to approach the operating conditions slowly, and to allow all internal ceramic tubes to reach an equilibrium operating temperature before the start of an experiment.

During the experiments with nitrous oxide, the heaters were brought up to the temperature control point and stabilized by means of an internal air flow which produced constant wall temperatures. After a steady air temperature was obtained, the air flow was terminated and nitrous oxide was introduced. Nitrous oxide flow rates from 1 to 2-1/2 liters/second have been utilized to date, at an internal pressure level of 10 atmospheres. The results obtained are shown in Table II.

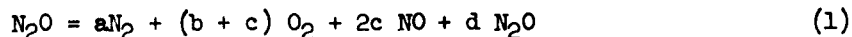
Initial experiments were initiated with a wall temperature of 925°K. At this temperature and pressure level, the estimated half-life of the nitrous oxide decomposition is approximately 600 seconds. An extremely rapid decomposition reaction occurred immediately after introduction of the nitrous oxide into the heaters. Gas temperatures at the outlet of the heater fluctuated between 1000°K and 2300°K. The final steady gas temperature at the exit of the heated section was 1500°K. The analysis of the gas composition at the exit of the heater showed that 96% of the nitrous oxide had decomposed. Local hot spots may have led to the premature decomposition of the nitrous oxide.

It has been determined definitely that a completely self-sustaining decomposition reaction was achieved, at the flow rates and pressure levels considered above without the use of a reaction initiator. After the stable gas temperature had been established, all electrical energy input to the heaters was turned off. The heater wall temperature continued to increase due to the heat transfer from the reacting gas to the heater walls. The increasing wall temperature continued to accelerate the decomposition reaction.

Subsequent experiments at lower initial temperatures indicate that the apparently anomalous results obtained for the conditions given above may have been caused by higher temperatures of some parts of the heater.

APPENDIX

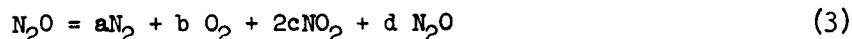
It is assumed that at high temperatures the decomposition of nitrous oxide leads to the following products only



However, in the presence of free oxygen, nitric oxide will form nitrogen dioxide at room temperature



so that at room temperature we may find only



For the analysis we use the fact that the nitrogen/oxygen atom ratio must remain constant. Also, we eliminate the NO_2 from the mixture by cold trapping it.

The resulting expressions for the percent by volume of the various species at elevated temperatures are:

$$\% \text{N}_2 = \frac{a}{2a - b + d} \quad (4)$$

$$\% \text{O}_2 = \frac{1}{3} \frac{(a + b)}{2a - b + d} \quad (5)$$

$$\% \text{NO} = \frac{2/3 (a - 2b)}{2a - b + d} \quad (6)$$

$$\% \text{N}_2\text{O} = \frac{d}{2a - b + d} \quad (7)$$

The overall area response of the chromatograph detector to various species is essentially linear for the sample sizes considered. The response can be written as

$$v_i = K_i A_i \quad (8)$$

where v_i is the volume of the i -th species in the sample, K_i is the correction factor for thermal conductivity, and A_i is the integrated area of the detector output response curve.

Combining (4), (5), (6), (7) and (8) and normalizing with respect to the nitrous oxide response, the percent composition of the species can be expressed as

$$\% N_2 = \frac{\frac{K_{N_2} A_{N_2}}{K_{N_2O} A_{N_2O}}}{D}$$

$$\% O_2 = \frac{\frac{1}{3} \frac{K_{N_2} A_{N_2} + K_{O_2} A_{O_2}}{K_{N_2O} A_{N_2O}}}{D}$$

$$\% NO = \frac{\frac{2}{3} \frac{K_{N_2} A_{N_2} - 2K_{O_2} A_{O_2}}{K_{N_2O} A_{N_2O}}}{D}$$

$$\% N_2O = \frac{1}{D}$$

where

$$D = \frac{2 K_{N_2} A_{N_2} - K_{O_2} A_{O_2}}{K_{N_2O} A_{N_2O}} + 1$$

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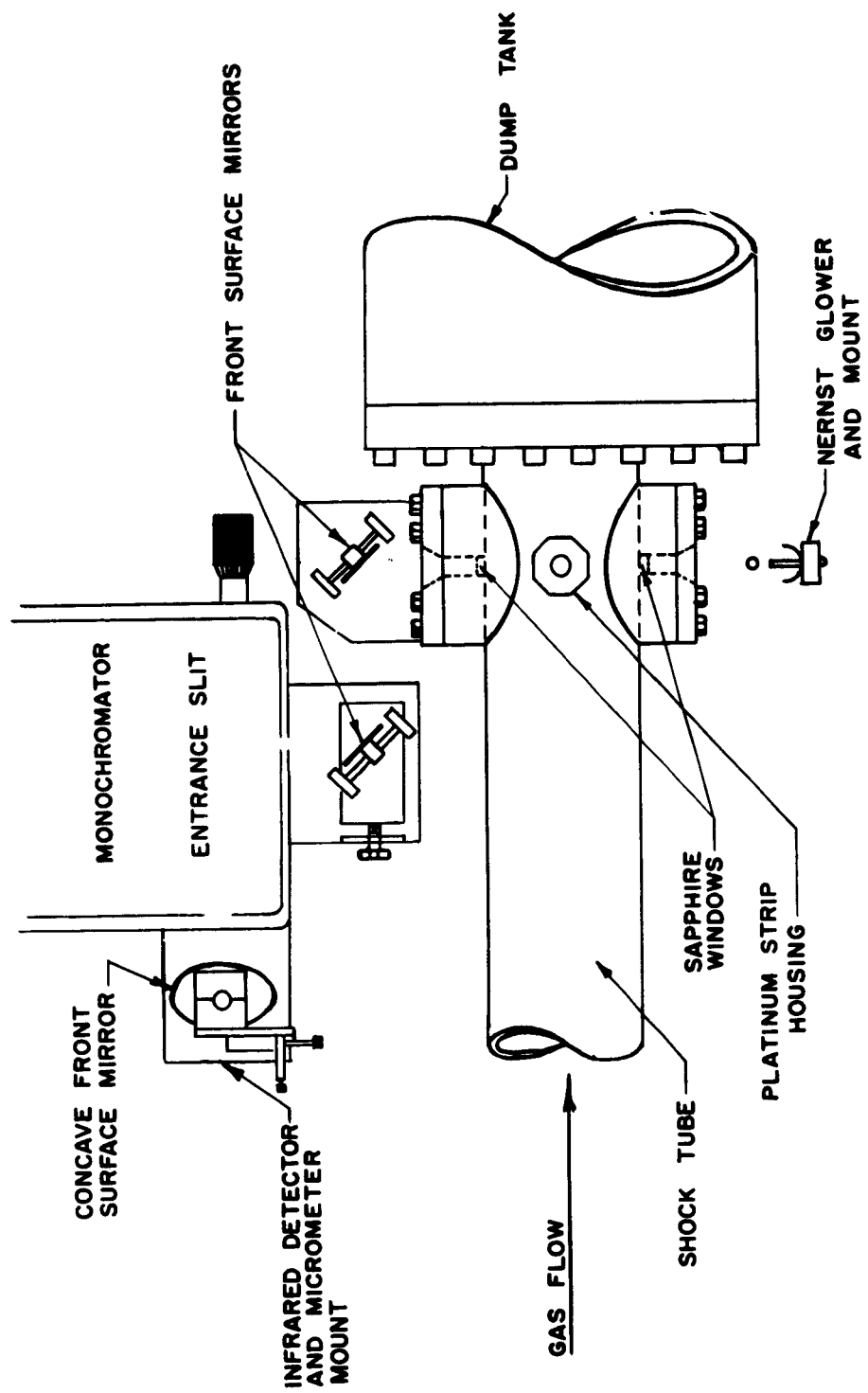
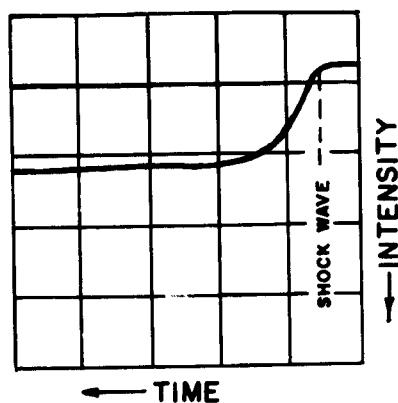
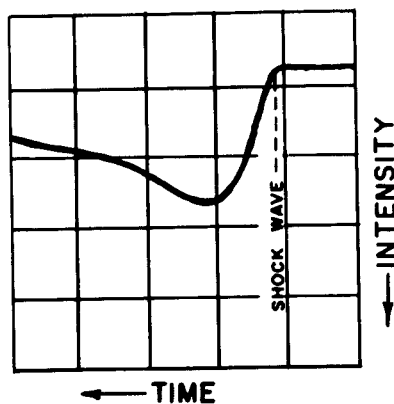


FIG. 1 INFRARED OPTICAL SYSTEM



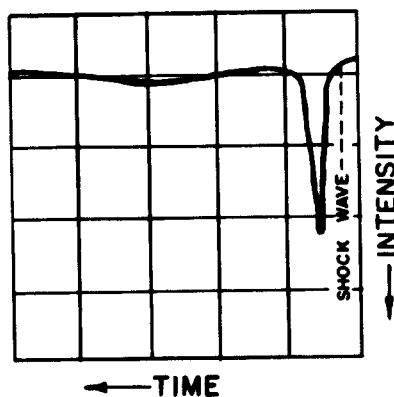
(a)

$T = 1160^{\circ}\text{K}$
 $P = 6.2 \text{ ATM.}$
 $95\% \text{ A} + 5\% \text{ N}_2\text{O}$
 NO DECOMPOSITION
 $200 \mu \text{ SEC. / DIV.}$



(b)

$T = 1440^{\circ}\text{K}$
 $P = 7.8 \text{ ATM.}$
 $95\% \text{ A} + 5\% \text{ N}_2\text{O}$
 $\text{HALF LIFE} = 1140 \mu \text{ SEC.}$
 $200 \mu \text{ SEC. / DIV.}$



(c)

$T = 2100^{\circ}\text{K}$
 $P = 16.3 \text{ ATM.}$
 $95\% \text{ A} + 5\% \text{ N}_2\text{O}$
 $\text{HALF LIFE} = 48 \mu \text{ SEC.}$
 $200 \mu \text{ SEC. / DIV.}$

FIG. 2 TYPICAL TRACES SHOWING DECOMPOSITION

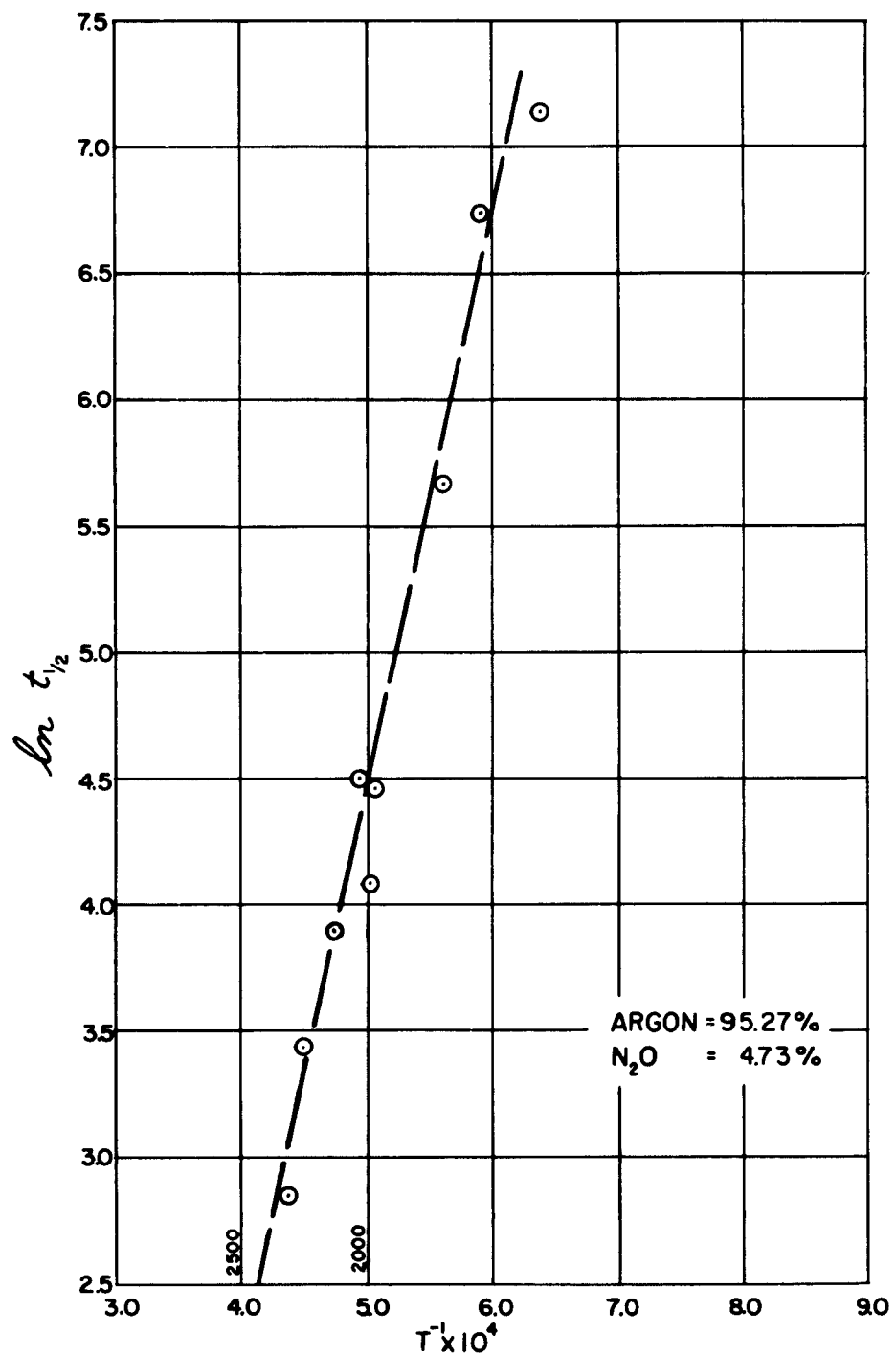


FIG. 3. HALF LIFE OF NITROUS OXIDE IN A NITROUS OXIDE - ARGON MIXTURE.

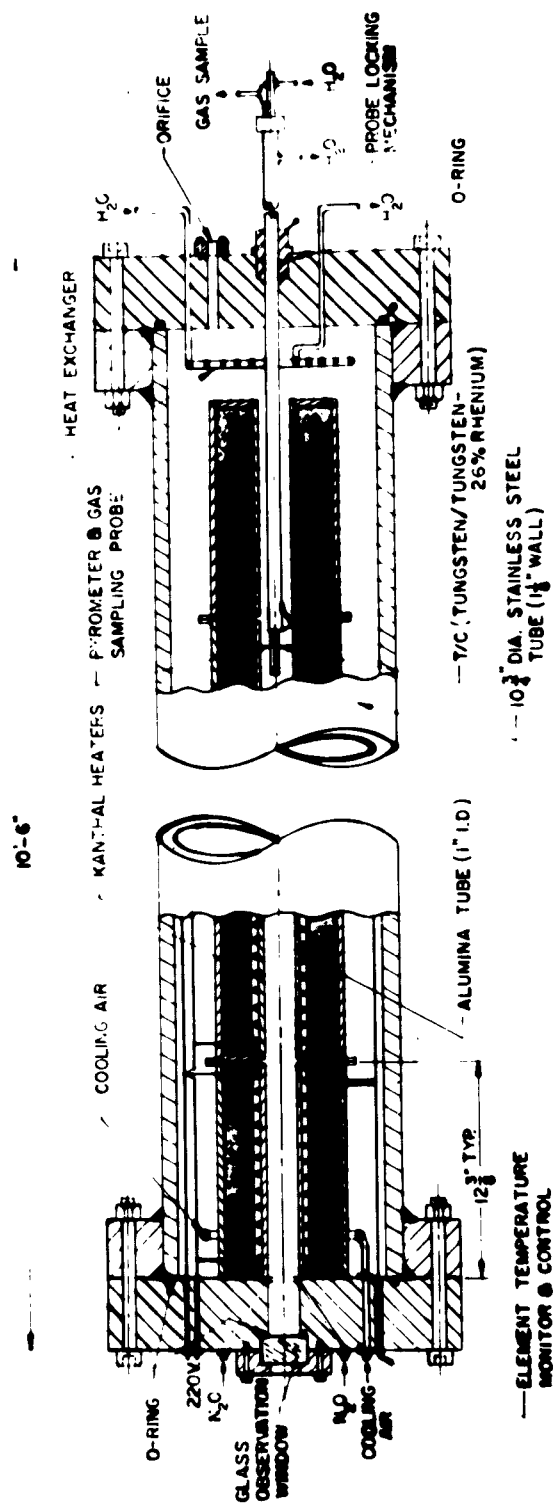
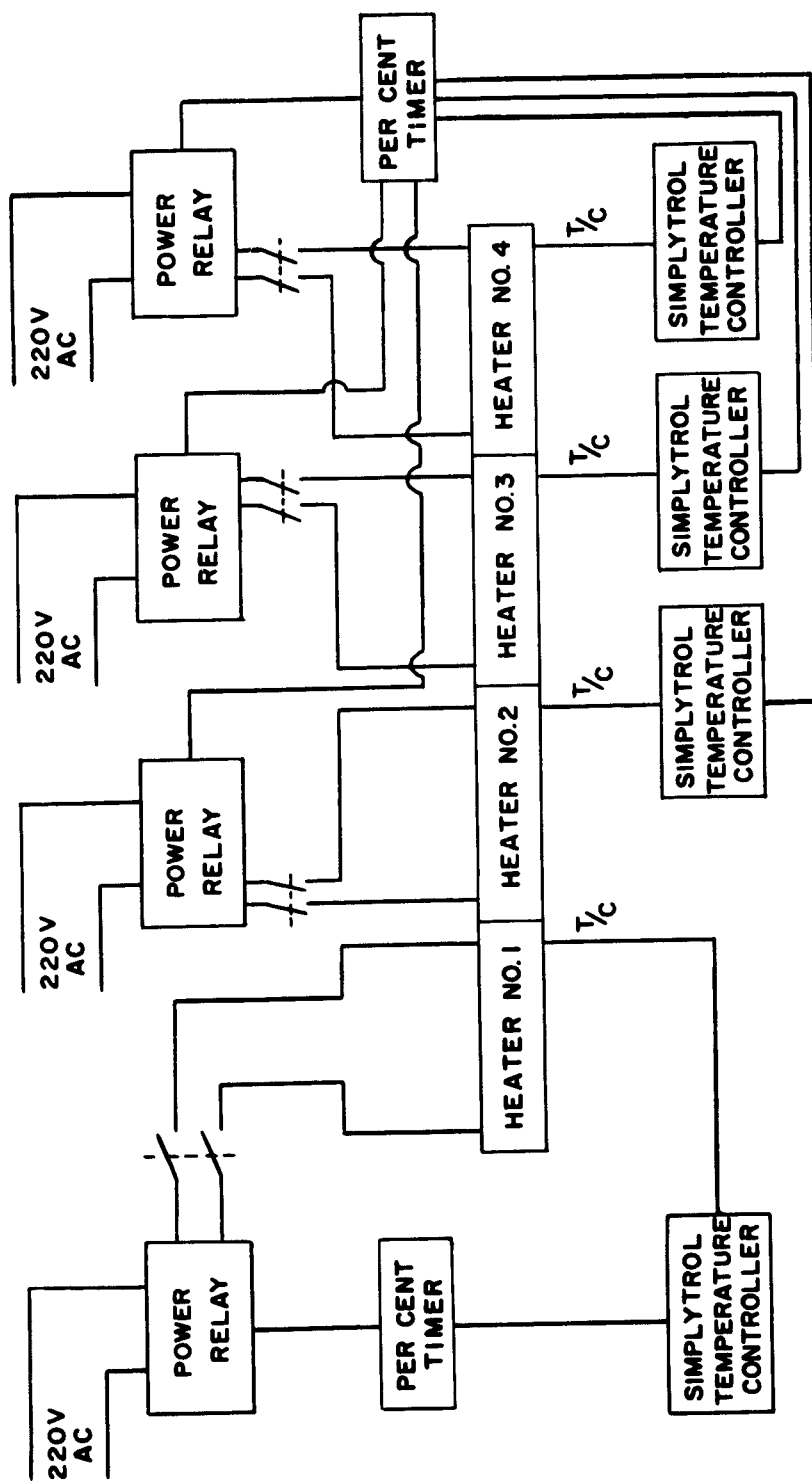


FIG. 4 REACTION VESSEL



NOTE:
T/C — CHROMEL/ALUMEL THERMOCOUPLE

FIG. 5 SCHEMATIC DIAGRAM OF TEMPERATURE CONTROL SYSTEM

TABLE I
EXPERIMENTAL RESULTS OF NITROUS OXIDE DECOMPOSITION
(4.63% N₂O + 95.27% A)

Gas Temperature (°K)	Gas Pressure (atm)	Half-Life of Nitrous Oxide (Microseconds)
1570	8.8	1290
1685	13.0	870
1800	8.3	240
1985	11.6	88
2000	10.9	59
2040	12.0	90
2100	16.3	48
2210	8.6	31
2290	14.0	18

TABLE II
CONSTANT PRESSURE DECOMPOSITION REACTION

PROBE LOCATION - HEATER EXIT

PRESSURE - 150 psig

Wall Temperature (°K)	Flow Rate (l/sec)	% N ₂ by volume	% O ₂ by volume	% NO by volume	% N ₂ O by volume	Gas Temperature (°K)
673	1.0	.18	.08	.06	99.68	703
723	1.0	.19	.07	.10	99.64	756
773	1.0	.22	.08	.10	99.60	846
823	1.0	.11	.04	.06	99.79	898
	1.0	1.02	.44	.30	98.24	888*
873	1.0	1.58	.62	.69	97.12	918*
923	2.5	61.42	29.19	6.08	3.31	1493

* Probe Thermocouple Failed During These Experiments